2-Indolyl Phenyl Ketone (22) from 18.—A suspension of **18** (0.18 g, 0.50 mmol) in 8 ml of ethanol and 2 ml of 2 *N* sodium hydroxide was refluxed for 2 hr. The reaction mixture was diluted with water and **22** was isolated by extraction with chloroform (0.107 g, 97%). The melting point and infrared spectrum were identical with those of pure **22**.

2-Indolyl 3-Pyridyl Ketone (24) from 19.—A suspension of **16** (7.6 g, 21 mmol) in a solution of 200 ml of methanol and 40 ml of 2 *N* sodium hydroxide was refluxed until hydrolysis was complete (20 hr). The solution was adjusted to pH 8 and the methanol was evaporated. Extraction with methylene chloride gave **24** (6.3 g, 83%), mp 166–171°, having an infrared spectrum identical with that of pure **24**.

Acknowledgment.—This research was supported by NSF Grant GP-19374 and by NCI Grant 1A12940-01.

Registry No.—**1a**, 40899-68-1; **1b**, 40899-69-2; **1c**, 3377-71-7; **1d**, 40899-71-6; **1e**, 17983-42-5; **1f**, 40899-73-8; **2**, 40899-74-9; **3**, 40899-75-0; **4**, 40899-76-1; **5**, 40899-77-2; **6**, 40899-78-3; **7**, 40899-79-4; **8**, 40899-80-7; **9**, 40899-81-8; **10**, 40899-82-9; **11**, 40899-83-0; **12**, 40899-84-1; **13**, 40899-85-2; **14**, 40899-86-3; **15**, 40899-87-4; **16**, 40899-88-5; **17**, 40899-89-6; **18**, 40899-90-9; **19**, 40899-91-0; **20**, 40899-92-1; **21**, 40899-93-2; **22**, 1022-86-2; **24**, 40899-94-3; **25**, 24512-42-3; **26**, 40899-96-5; **27**, 40899-97-6; **28**, 40899-98-7; **29**, 40899-99-8; **30**, 40900-00-3; **31**, 40900-01-4; 2-LiMMI, 40900-02-5; 2-LiBSI, 40900-03-6; indole, 120-72-9; methoxymethyl chloride, 107-30-2; benzyloxymethyl chloride, 3587-60-8; benzyl chloride, 100-44-7; benzenesulfonyl chloride, 98-09-9; trimethylchlorosilane, 75-77-4; *tert*-butyldimethylchlorosilane, 18162-48-6; *N*-methylformanilide, 93-61-8; benzonitrile, 100-47-0; 4-methoxybenzonitrile, 874-90-8; 2-cyanopyridine, 100-70-9; 4-cyanopyridine, 100-48-1; benzaldehyde, 100-52-7; 4-methoxybenzaldehyde, 123-11-5; pyridine-2-carboxaldehyde, 1121-60-4; acetophenone, 98-86-2; 4-methoxyacetophenone, 100-06-1; 4-acetylpyridine, 1122-54-9; benzoyl chloride, 98-88-4; nicotinoyl chloride, 10400-19-8; ethyl chloroformate, 541-41-3; ethyl benzoate, 93-89-0; ethyl nicotinate, 614-18-6.

Syn–Anti Isomerization of *N*-(*p*-Tolyl)imines of Ferrocenyl, Ruthenocenyl, and (Cyclobutadienyliron Tricarbonyl) Phenyl Ketones

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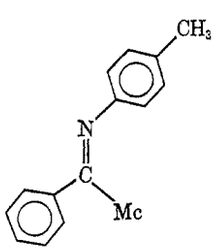
The *N*-(*p*-tolyl)imines of ferrocenyl, ruthenocenyl, and (cyclobutadienyliron tricarbonyl) phenyl ketones were prepared in moderately good yield. Studies of their syn–anti isomerization using the dnmr technique allowed the determination of their free energies of activation. The validity of approximate equations to determine free energies of activation as well as the conditions necessary for successful complete line-shape analysis are discussed.

Recently we reported[1] evidence for the syn–anti isomerization of imines I and II. In that report we

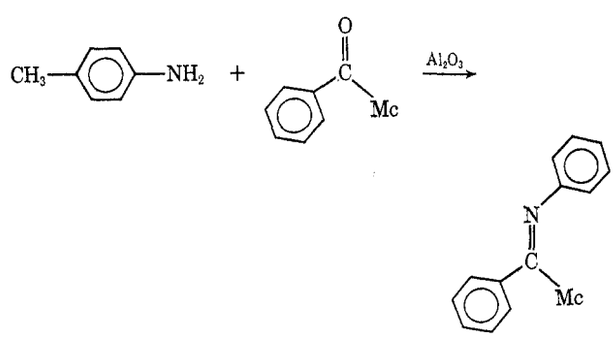


I, Mc = ferrocenyl
II, Mc = ruthenocenyl
III, Mc = cyclobutadienyliron tricarbonyl

drew attention to the approximate nature of the dnmr measurements used as supporting evidence for the isomerization. In this paper we not only extend our measurements to compound III, but also bring to light our attempts to apply complete line-shape analysis to the dynamic nuclear magnetic resonance (dnmr) data. In addition, the preparations of compounds I, II, and III are discussed.

Results and Discussion

The three compounds used in this study were prepared using the method of Hetnarski and Grabowski[1,2] in which *p*-toluidine and the appropriate phenone compound were condensed in the presence of aluminum oxides. This method originally had been successfully applied[2] only to ferrocene derivatives. We have expanded the method's utility and it appears to be fairly



general for the reaction of metallocene and metallocene-like ketones with aromatic amines. The beauty of the method is that it can be carried out under mild conditions (refluxing toluene), that it is quite clean (followed by thin layer chromatography), and that work-up is fairly simple. Purified yields range from 40 to 50%.

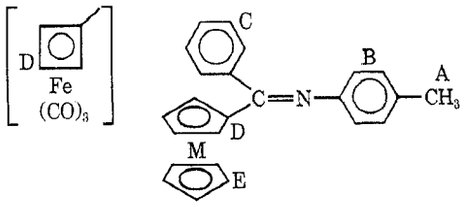
Characterization of I–III was accomplished using infrared, mass, and nuclear magnetic resonance spectroscopy and elemental analysis. Examination of both ir and nmr spectra made it clear that a mixture of isomers had been obtained. As examples: Compound I and II have doubled signals of unequal intensity assigned to the *p*-methyl group and to the unsubstituted cyclopentadienyl hydrogens. Compound III has two signals for its *p*-methyl group as well as doubled signals in the cyclobutadienyl group. It should be noted that we have observed other signal doubling, but that it occurs with protons of low intensity and high splitting and is consequently less dramatic. In Table I we have compiled the nmr data for compounds I–III. The unequal intensities of the signals indicated in Table I show that in compounds I and II one isomer predominates by six- to tenfold while the isomer ratio in III is

(1) R. Damrauer and T. E. Rutledge, *J. Organometal. Chem.*, **29**, C 9 (1971).

(2) B. Hetnarski and Z. Grabowski, *Bull. Acad. Pol. Sci.*, **17**, 391 (1969).

TABLE I

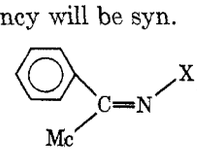
ROOM-TEMPERATURE NMR SPECTRA OF I, II, AND III



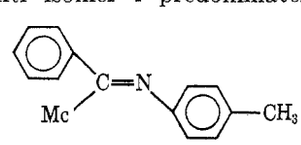
	A[a,b]	B	C	D	E
I	2.17 (s) [10][c]			4.38 (t)	4.12 (s) [7]
	2.37 (s) [1]	6.70 (q)	7.20 (s)	4.65 (t)	4.22 (s) [1]
II	2.16 (s) [6]			4.70 (t)	4.62 (s) [6]
	2.30 (s) [1]	6.67 (q)	7.15 (s)	4.93 (t)	4.53 (s) [1]
III	2.18 (s) [1]		6.68 (s)	3.67 (s)	
			7.17 (m)	4.07 (s)	
	2.35 (s) [1.3]	6.62 (q)	7.43 (m)	4.32 (s)	
				4.48 (s)	

[a] δ in parts per million downfield from TMS; $CDCl_3$ solvent. [b] s = singlet, t = triplet, q = quartet, m = multiplet. [c] Relative intensities in brackets.

more nearly equal. To attempt to ascertain the identity of each isomer, we studied the solution and solid infrared spectra of I–III. Curtin and coworkers[3] have assigned the syn and anti configuration to isomers of benzophenone imines basing their judgment on the observation that in disubstituted olefins (styrene-like) the hydrogen deformation band of the monosubstituted phenyl ring occurs at higher frequency in that isomer with an atom or group cis to the phenyl ring. As applied to imines the isomer with the higher hydrogen deformation frequency will be syn. Applying Curtin's



criterion to compounds I and II it would appear as though the anti isomer i predominates in solution



i

(Table II). We are hesitant to accept this based on earlier work[4] in which the bulkiness of the ferrocenyl

TABLE II

INFRARED STRETCHING FREQUENCIES OF I, II, AND III IN THE 700-CM^{-1} REGION

	Solution (CS_2), cm^{-1}		Solid (KBr), cm^{-1}	
I	693 (m)[a]	703 (sh)	702 (m)	714 (s)
II	692 (m)	699 (sh)	701 (m)	710 (s)
III	700 (s)	720 (vw)	690 (s)	702 (vw)

[a] sh = shoulder, s = strong, m = medium, vw = very weak.

group was shown to be an important factor in determining the dynamic processes of ferrocenyl amides. It seems prudent to state that, although it is quite clear that one isomer predominates in I and II (and it appears to be the same isomer), we are not convinced that Curtin's criterion applies to compounds I–III. The solid-phase infrared results (Table II) further complicate isomeric assignment since in these the intensities of the predominant peaks are reversed.

To obtain information on the dynamics of the syn–anti isomerization process of I–III we studied their nmr spectra as a function of temperature. All of the spectral changes to be discussed have been shown to be reversible. We have witnessed a coalescence of all of the doubled signals mentioned previously, but for the purposes of dnmr analysis have focused our attention on the *p*-methyl group. The coalescence temperatures for compounds I–III are 54, 61, and 91°, respectively.

Since only few data[5,6] exist on the activation parameters for syn–anti isomerizations of ketimines, we have attempted complete line-shape analysis on compounds I–III. The introduction of experimental parameters into the standardly modified Block equations[7,8] generated a series of theoretical line shapes. These were visually[9] compared with the experimental curves, thus allowing rate constant assignment to the experimental data. Activation parameters generated by this method are compiled in Table III.[10] The entropies of activation are suspiciously large (in absolute value) for a process whose transition state does not involve either bond making or breaking or large changes in nonbonded interactions.[11] Raban and Carlson[11] in commenting upon the reliability of activation entropy data generated by complete line-shape analysis suggest that these data are highly suspect *unless* the temperature range over which the analysis is made exceeds 100°. Our data, obtained over a fairly small temperature range, appear unreliable in this respect. The free energies of activation, however, are indicative of the now common experience[11] that complete line-shape analysis provides quite reasonable free energies of activation.

TABLE III

ACTIVATION PARAMETERS BY VISUAL CORRELATION OF EXPERIMENTAL DATA AT 25°

Compd	$\Delta H^{\ddagger}$, kcal/mol[a]	$\Delta S^{\ddagger}$, eu	$\Delta G^{\ddagger}$, kcal/mol	K[b]
I	27.0	25.1	19.6	0.14
II	23.7	14.7	19.3	0.15
III	17.6	−8.6	20.2	1.28

[a] k_A for A → B. [b] $K = P_B/P_A$ where A is upfield of B, and P_A is the population of A.

Because of our failure to obtain reliable activation entropies for the syn–anti isomerization process, we explored the utility of the approximate equations in evaluating $\Delta G^{\ddagger}$ at the coalescence temperature. Table IV details the results of calculations carried out by two approximation procedures.[12,13] The first[12] strictly applies only to unsplit coalescing signals of equal

(3) (a) D. Y. Curtin and J. W. Hausser, *J. Amer. Chem. Soc.*, **83**, 3474 (1961); (b) D. Y. Curtin, E. J. Grubbs, and C. G. McCarty, *J. Amer. Chem. Soc.*, **88**, 2775 (1966).

(4) R. Damrauer, *J. Organometal. Chem.*, **32**, 121 (1971).

(5) C. G. McCarty in "The Chemistry of the Carbon–Nitrogen Double Bond," S. Patai, Ed., Wiley-Interscience, New York, N. Y., 1970.

(6) H. Kessler, *Angew. Chem., Int. Ed. Engl.*, **9**, 219 (1970).

(7) H. S. Gutowsky and C. H. Holm, *J. Chem. Phys.*, **25**, 1228 (1956).

(8) G. Binsch, *Top. Stereochem.*, **3**, 97 (1968).

(9) A program to normalize experimental curves for easy visual comparison with theroetical curves was used. Computer-aided least square fitting of experimental and theroetical data did not improve on visual data comparison.

(10) See paragraph at end of paper regarding supplementary material.

(11) M. Raban and E. Carlson, *J. Amer. Chem. Soc.*, **93**, 685 (1971).

(12) D. Kost, E. H. Carlson, and M. Raban, *Chem. Commun.*, 656 (1971).

(13) H. Shanan-Atidi and K. H. Bar-Eli, *J. Phys. Chem.*, **74**, 961 (1970).

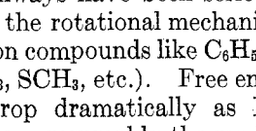
TABLE IV
COMPARISON OF FREE ENERGIES[a] OF ACTIVATION DETERMINED BY VARIOUS METHODS

	Visual[b] complete line shape at T_c	Approximate[c] expression at T_c	Approximate[d] expression at T_c
I	18.9	17.2	18.2
II	18.8	17.6	18.4
III	20.8	19.0	19.0

[a] In kcal/mol. [b] A → B from rate constants expressed in radians/sec. [c] $\Delta G^{\ddagger}$ at $T_c = -RT \ln [k_c h/kT_c]$; $k_c = \pi\Delta\nu/\sqrt{2}$. [d] See H. Shanan-Atidi and K. H. Bar-Eli, *J. Phys. Chem.*, **74**, 961 (1970).

intensity while the latter[13] has been applied to unsplit signals of unequal intensity. It is clear from the table that the latter, the method of Shanan-Atidi and Bar-Eli,[13] gives results more closely in agreement with the complete line-shape results. However, the uncertainties resulting from the small temperature range studied for compounds I–III indicate that the complete line-shape analysis offers no advantage over the approximate methods. The similar $\Delta G^{\ddagger}$ values for the three methods in Table IV give us confidence in their validity, as does the now common experience of such similarities in others' analyses.[11,12]

Studies relating to the mechanism(s) of syn–anti isomerization of imines are numerous.[5] Two limiting mechanisms have been considered seriously with imines: (1) a lateral shift or inversion mechanism through a linear, –N=C<, transition state and (2) a rotational mechanism with a transition state resembling either –Ṅ–Ċ< or $-N^{-}-C^{+}<$. In the lateral shift the substituent on nitrogen shifts from one isomeric environment to the other while the π bond remains intact and nitrogen rehybridizes to sp in the transition state; the rotational mechanism occurs through the "single-bonded" transition state by "free" rotation. Because the activation energies necessary for a homolytic rotational isomerization are expected to be high, it is generally thought[5] that such a pathway is unlikely for most imines. Both the heterolytic rotational and lateral shift pathways have been seriously considered. Evidence[14,15] for the rotational mechanism rests on substituent studies on compounds like $C_6H_5N{=}CX_2$ (where X = CH_3, OCH_3, SCH_3, etc.). Free energies of activation ($\Delta G^{\ddagger}_{T_c}$) drop dramatically as X's conjugative ability increases as presumably the mechanism shifts to purely rotational. The $\Delta G^{\ddagger}$'s range from 21 kcal/mol for a carbon to 12 kcal/mol for a nitrogen substituent. The lateral shift mechanism[3,5] appears to operate with compounds like ii. Substituents X and Y have very



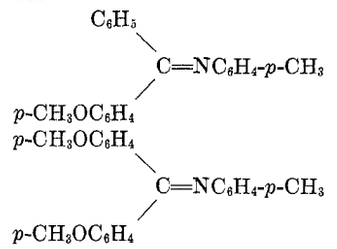
ii

small effects on activation energies (ρ = 0.1) while Z's effects (ρ = 1.5) are only slightly larger.[3] In all, E_a's between 17 and 20 kcal/mol are obtained.

Since no well-substantiated case for a rotational mechanism exists when X is a carbon substituent, we decided to attach to this position a metallocene group. We chose the ferrocenyl, ruthenocenyl, and cyclobutadienyliron tricarbonyl compounds I–III because we felt that the well-known[16–19] tendency of these to stabilize an adjacent electron-deficient center would stabilize a dipolar transition state like $>C^{+}-N^{-}-$. In addition, we designed compounds I–III to be comparable with the isomerization data of other imines.[3]

Table V summarizes our data as well as some of that of Curtin and coworkers[3] on the isomerization of

TABLE V
FREE ENERGIES OF ACTIVATION[a] OF VARIOUS PHENONES

Compd	$\Delta G^{\ddagger}$[b] at T_c
I	18.2
II	18.4
III	19.0
	18.5
	18.8

[a] A → B from rate constants expressed in radians/sec. [b] See H. Shanan-Atidi and K. H. Bar-Eli, *J. Phys. Chem.*, **74**, 961 (1970).

phenone arylimines (made comparable by recalculating Curtin's data[3,12,13]); although there are slight variations among results, they are not considered to be significant in view of the rather substantial variations we have seen earlier in treating the data using various methods of analysis. We believe, therefore, that the free energies of all five compounds listed in Table V are substantially the same and that the effect of the metallocene or metallocene-like substituent is not noticeably different from that of an aromatic substituent. As a result we feel that these groups are not in any perceptible way stabilizing a dipolar rotation transition state. We conclude based on our data and its comparison to that of Curtin that the syn–anti isomerization for compounds I–III occurs through a lateral shift mechanism.

Experimental Section

General Comments.—Elemental analyses were performed by Huffman Laboratories, Wheatridge, Colo. Ir spectra were recorded using either a Perkin-Elmer 237B grating ir spectrophotometer or a Beckman IR-12. The nmr spectra were recorded using a Varian A-60A high-resolution spectrometer. Chemical shifts are reported in parts per million downfield from tetramethylsilane. All nmr temperature studies were performed using a Varian Associates 6040 variable temperature controller on degassed samples under prepurified nitrogen. Temperature measurements were made using either the methanol (<30°) or ethylene glycol (>30°) separation–calibration method. Such measurements were carried out before and after each temperature run. Mass spectra were recorded on an AEI MS-12 mass spectrometer. All reactions were carried out under an atmosphere of prepurified nitrogen. Boiling points were recorded at prevailing pressure (~640 mm) unless otherwise indicated. Boiling and melting points are uncorrected.

(14) N. P. Marullo and E. H. Wagener, *Tetrahedron Lett.*, 2555 (1969).
(15) M. Raban, *Chem. Commun.*, 1415 (1970).
(16) E. A. Hill and R. Wiesner, *J. Amer. Chem. Soc.*, **91**, 509 (1969).
(17) M. Cais, *Rec. Progr.*, **27**, 177 (1966).
(18) S. P. Gubin and A. A. Lubovick, *J. Organometal. Chem.*, **22**, 183 (1970).
(19) L. Watts, Jr., Ph.D. Dissertation, University Microfilm Inc., Ann Arbor, Mich., 1966, No. 66-7383.

Preparation of the *N*-(*p*-Tolyl)imine of Ferrocenyl Phenyl Ketone (I).—Into a single-necked 50-ml flask equipped with a condenser, nitrogen inlet tube, and magnetic stirring bar were charged 0.25 g (0.86 mmol) of benzoylferrocene (Arapahoe Chemical Co.), 0.10 g (0.95 mmol) of *p*-toluidine [sublimed at 40° (0.01 mm) from Eastman Practical], 97 mg (0.95 mmol) of aluminum oxide (Merck acid washed), and 25 ml of dry toluene. The mixture was refluxed for 4 days; daily additions of 0.1 g of *p*-toluidine were required to maximize the rate of formation of imine. Monitoring by thin layer chromatography indicated that an equilibrium mixture had formed after 4 days. The hot reaction mixture was filtered through a sintered glass funnel and the filtrate yielded a red residue (0.42 g) upon rotary evaporation at 50° (15 mm). Addition of hexane cause the residue to crystallize. Excess *p*-toluidine was removed by sublimation at 40° (0.01 mm). Column chromatography using benzene as eluent yielded 0.27 g (83%) of imine (fastest moving band) as well as some unreacted ketone.

A large-scale experiment carried out on 9.20 g (31.6 mmol) of benzoylferrocene yielded 5.0 g (42%) of pure imine (recrystallization from hexane gave mp 138–139°): ir ($CDCl_3$) 3107, 3080, 2941, 2880, 1605, 1591, 1575, 1494, 1452, 1285, 1097, 944, 958, 917, and 872 cm^{-1}; nmr ($CDCl_3$), see Table I; mass spectrum (70 eV) *m/e* (rel intensity) 381 (4), 380 (31), 379 (100), 378 (10), 377 (12), 314 (29), 121 (10), and 69 (10).

Anal. Calcd for $C_{24}H_{21}FeN$: C, 76.00; H, 5.58. Found: C, 75.83; H, 5.71.

Preparation of the *N*-(*p*-Tolyl)imine of Ruthenocenyl Phenyl Ketone (II).—Into a 250-ml single-neck flask equipped with a condenser, nitrogen inlet tube, and magnetic stirring bar were charged 2.86 g (8.5 mmol) of ruthenocenyl phenyl ketone,[20] 2.74 g (25.6 mmol) of *p*-toluidine (Eastman Practical, recrystallized), 8.72 g (85.4 mmol) of aluminum oxide, and 100 ml of dry toluene. Thin layer monitoring showed after reflux for 2 days that the reaction was complete. The mixture was filtered through a sintered glass filter and rotary evaporated. Addition of petroleum ether caused the residue to crystallize. Unreacted *p*-toluidine was removed by sublimation at room temperature (0.05 mm) and the sublimation residue was chromatographed on alumina. With benzene as eluent three bands were readily distinguishable and separable. The fastest moving was ruthenocene, the next, the imine, and the slowest, ruthenocenyl phenyl ketone. We obtained 0.65 g (23%) of starting ketone as well as 1.66 g (47%) of the imine after recrystallization from petroleum ether: mp 100–101°; ir ($CDCl_3$) 3100, 2977, 1608, 1491, 1286, 1094, 997, 974, 878, and 864 cm^{-1}; nmr ($CDCl_3$), see Table I; mass spectrum (70 eV) *m/e* (rel intensity) 429 (3), 428 (16), 427 (50), 426 (36), 425 (100), 424 (88), 423 (78), 422 (63), 421 (28), 420 (11), 419 (14), 319 (20), 231 (14), 195 (11), 194 (55), and 167 (15).

Anal. Calcd for $C_{24}H_{21}RuN$: C, 67.91; H, 4.99. Found: C, 68.16; H, 5.24.

Preparation of the *N*-(*p*-Tolyl)imine of (Cyclobutadienyliron Tricarbonyl) Phenyl Ketone (III).—(Cyclobutadienyliron tricarbonyl) phenyl ketone[19] (5.0 g, 16.9 mmol), 5.44 g (50.8 mmol) of *p*-toluidine, 17.2 g (169 mmol) of aluminum oxide, and 100 ml of toluene were allowed to react at reflux for 3 days. The reaction and work-up were essentially the same as those described to prepare I and II with the following exceptions: (1) the reaction vessel was protected from light by aluminum foil; (2) chromatographic separation with benzene yielded in the initial fractions a mixture of starting ketone, *p*-toluidine, and imine; (3) sublimation at 30° (0.02 mm) removed ketone and *p*-toluidine; and (4) further sublimation at 60–80° (0.02 mm) yielded yellow crystals of imine. A total yield of 3.0 g (46%) of imine III was obtained: mp 110–112°; ir ($CDCl_3$) 3300, 2050, 1975, 1605, 1100, 1005, 925, and 810 cm^{-1}; nmr ($CDCl_3$), see Table I; mass spectrum (70 eV *m/e* (rel intensity) 386 (1), 385 (4), 357 (36), 329 (22), 302 (18), 301 (77), 276 (21), 275 (100), 194 (16), 173 (29), 172 (17), and 81 (10).

Anal. Calcd for $C_{21}H_{15}O_3NFe$: C, 65.48; H, 3.93. Found: C, 65.62; H, 4.17.

Comments on Variable-Temperature Nmr Studies and Analysis of Data.—Solvents used for the variable-temperature measurements (diphenyl ether and α,α,α-trifluorotoluene) showed only very slight shifts relative to $CDCl_3$. Slight discrepancies between the data in Table I and our preliminary report[1] are caused by the solvent effects. The necessary precautions for accurate dnmr work were taken[8,21] both with respect to the experimental measurements and analysis of the data.

Acknowledgments.—We would like to thank the Arapahoe Chemical Co. for gifts of ruthenocene and benzoylferrocene. We also acknowledge the support of the Research Corporation, the National Institutes of Health (through a Biomedical Grant administered by the University), the American Cancer Society (through a grant administered by the University of Colorado Medical School), the Graduate School of the University of Colorado, and University of Colorado Computing Center. Finally, we thank Professor S. Zumdahl for supplying us with the dnmr programs as well as much valuable information about their proper use.

Registry No.—*syn*-I, 40940-71-4; *anti*-I, 40940-73-6; *syn*-II, 40940-74-7; *anti*-II, 40940-75-8; *syn*-III, 40940-76-9; *anti*-III, 40940-72-5.

Supplementary Material Available.—Nmr spectra at varying temperatures will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 20 × reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche, referring to code number JOC-73-3330.

(20) M. D. Rausch, E. O. Fischer, and H. Gurbert, *J. Amer. Chem. Soc.*, **82**, 76 (1960).

(21) A. Allerhand, H. S. Gutowsky, J. Jonas, and R. A. Meinzer, *J. Amer. Chem. Soc.*, **88**, 3185 (1966).